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A Chemical Device That Exhibits Dual Mode Motions: Dynamic Coupling of Amide Coordination Isomerism and Metal-Centered Helicity Inversion in a Chiral Cobalt(II) Complex

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Dynamic and consecutive molecular motions such as stretching, winding, and rotation are observed in nature. The ATP-driven F1 part of ATP synthase[1a] and the bacterial flagellar motor[1b] are typical examples, in which some external stimuli kick-off such events through conformational changes of biopolymers. Several molecular machines such as molecular rotors, gears, and shuttles have recently been developed, in which metal-coordination linkage isomerizes dynamically to offer single mode motion.[2] Since the planar amide linkage (-CO-NH-) has two preferred structures (*cis*–*trans* isomers) and two different metal coordination modes (O-coordination and N-coordination),[3] its isomerism is often used to alter the three-dimensional structures of biological proteins. Herein, we develop a chemical device based on a chiral Co^{II} complex that exhibits dual mode motions. The ligand employed here (H_2**L1**) includes 2,5-dimethoxy benzene moieties attached through amide linkages to both terminals of a helical tetradentate ligand. The acid–base reaction of the corresponding cobalt complex triggered the interconversion of coordinating atoms between amide nitrogen atoms and amide oxygen atoms, giving rise to a stretching (extension/contraction) molecular motion. Since we previously demonstrated that the helicity of the Co^{II} complex with H_2**L2** was dynamically inverted from the Λ *cis*-α form to the Δ *cis*-α form by adding achiral NO_3^- ions,[4–6] the employed H_2**L1**-Co^{II} complex was designed to work as a novel type of molecular machine that exhibits coupled stretching and inverting motions. Several types of helical ligands have shown extension/contraction molecular motion on metal complexation/decomplexation[2d–e,7] and/or protonation/deprotonation,[7,8] but the present type of kinetically labile Co^{II} complex allows a dual molecular motion in a highly dynamic fashion, as would be required for a sophisticated supramolecular switching device.

As established for the H_2**L2**-$Co(ClO_4)_2$ complex,[4] X-ray analysis of the pink-colored H_2**L1**-$Co(CF_3SO_3)_2$ complex[9,10] and its solid-state CD studies[11] revealed that the complex had a Λ *cis*-α coordinated structure, in which two amine nitrogen atoms, two amide oxygen atoms, and two donors from solvent molecules and/or counter anions coordinated (see extended Λ-form in Figure 1, middle). ^{19}F NMR[12] and IR[13] studies in acetonitrile/chloroform (1/9) indicated that one $CF_3SO_3^-$ ion coordinated to the Co^{II} center, and one $CF_3SO_3^-$ ion remained noncoordinated, as observed in the solid state. Its diastereomeric excess (*de*) value in the solution was determined to be above 95 % on the basis of paramagnetic ^1H NMR spectra.[14] A green-colored Co^{II} complex was isolated by mixing H_2**L1** and $Co(ClO_4)_2 \cdot 6H_2O$ in the presence of two equivalents of $(C_2H_5)_3N$, and showed a characteristic CD spectrum in CH_3CN (see contracted Λ-form in Figure 1, left).[15] Two amine nitrogen, two amido nitrogen, and two methoxy oxygen atoms from the ligand coordinated to the Co^{II} center, to give overall a distorted octahedral geometry with contracted left-handed helical structure ($\Lambda_4\Delta_2$ absolute configuration between the skew chelate pairs[16]). In the ^1H NMR spectrum recorded in $CD_3CN/CDCl_3$ (1/9), all signals appeared in the region $\delta = -70$ to 110 ppm with C_2-symmetric patterns (see Figure S5 in the Supporting Information). Since no significant signals for the minor diastereomeric isomer were observed, it appears that this complex retains the contracted helical structure in the solution. The [Co(**L1**)] complex exhibited positive CD signals at 433 and 918 nm and negative signals at 474, 607, and 1100 nm in $CH_3CN/CHCl_3$ (1/9; Figure 2, ●), which has a pattern similar to that observed in the solid-state CD spectrum (see Fig-

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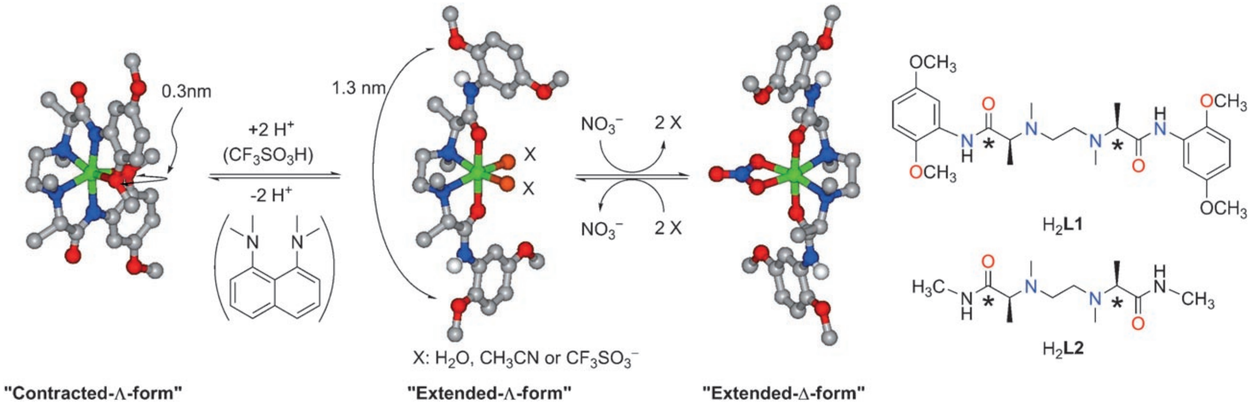


Figure 1. Stretching and inverting dual motions of the Co^{II} complex. Crystal structures of [Co(**L1**)] (left) and $[Co(H_2\mathbf{L1})(CF_3SO_3)(H_2O)](CF_3SO_3)\cdot(CHCl_3)$ (middle), and DFT-optimized structure of $[Co(H_2\mathbf{L1})(NO_3)]^+$ (right) are illustrated. Most hydrogen atoms, solvent molecules, and $CF_3SO_3^-$ ions are omitted for clarity.

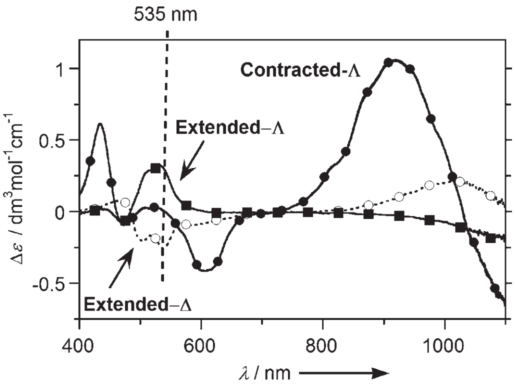


Figure 2. CD spectra of $[Co(H_2\mathbf{L1})(CF_3SO_3)(H_2O)](CF_3SO_3)\cdot(CHCl_3)$ (■), [Co(**L1**)] (●) and $[Co(H_2\mathbf{L1})(CF_3SO_3)(H_2O)](CF_3SO_3)\cdot(CHCl_3)$ in the presence of five equivalents of Bu_4NNO_3 (○) in $CH_3CN/CHCl_3$ (1/9) at room temperature. [complex] $= 2.5\times10^{-3}$ mol dm^{-3}, 10 mm cuvette.

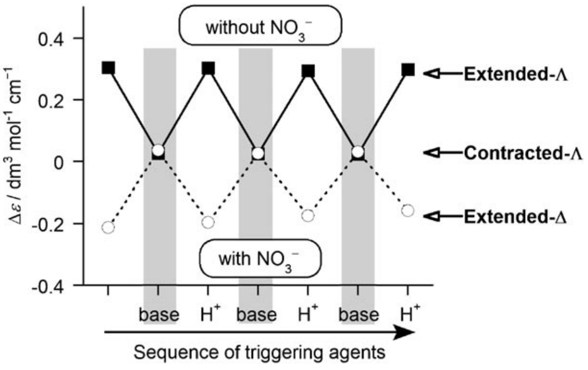


Figure 3. Protonation/deprotonation-induced reversible switching of the contracted-Λ/extended-Λ (■) and contracted-Λ/extended-Δ (○) process observed by CD spectra at 535 nm in $CH_3CN/CHCl_3$ (1/9). H^+: CF_3SO_3H; base: 1,8-bis(dimethylamino)naphthalene.

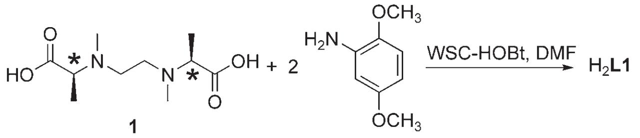
ure S2 in the Supporting Information). Upon addition of two equivalents of *N,N,N′,N′*-tetramethyl-1,8-naphthalenediamine (proton sponge) to the solution of the $[Co(H_2\mathbf{L1})(CF_3SO_3)(H_2O)]^+$ complex, the color of the solution changed from pink to green after stirring for 10 min, and its CD spectrum also changed to that observed for the [Co(**L1**)] complex.[17] When two equivalents of CF_3SO_3H were added to the green-colored solution, the color of the solution changed rapidly (ca. 5 s) to pink, and the sign of the CD signal appearing around 530 nm changed from approximately zero to positive (Figure 2, ■). Thus, protonation/deprotonation induced a stretching motion by means of amide coordination isomerism (amide N-coordination ↔ amide O-coordination). Since no significant decrease of CD intensity was observed after repeating the protonation/deprotonation several times (see Figure 3, ■), this stretching (extension/contraction) motion occurred reversibly.

Addition of five equivalents of Bu_4NNO_3 to the solution of the extended $[Co(H_2\mathbf{L1})(CF_3SO_3)(H_2O)]^+$ complex gave rise to a negative CD signal around 530 nm (Figure 2, ○), which was similar to that of the right-handed Co^{II} complex with H_2**L2**.[4] As previously established, bidentate chelation of the NO_3^- ion to the Co^{II} center and hydrogen bonding of the NO_3^- ion to the amide hydrogen atom cooperatively stabilized the Δ-form (see contracted Δ-form in Figure 1, right). A similar negative CD signal was observed when both two equivalents of CF_3SO_3H and five equivalents of Bu_4NNO_3 were added to the contracted [Co(**L1**)] complex, indicating that the contracted structure was extended, then its helical direction was inverted.[18]

As demonstrated above, the linkage isomerism of the amide group in the octahedral metal complex provides dynamic molecular motion between two distinct structures (contraction/extension), in which the distance between two coordinated methoxy oxygen atoms was changed from 0.3 nm to 1.3 nm. Furthermore, the direction of two coordinated methoxy groups (O-CH_3) was changed dramatically (Figure 1). Since the helical direction of the extended complex was further inverted in response to the NO_3^- ion, both stretching and inverting motions occurred reversibly and repeatedly (Figure 3). Thus, our complex can be considered as a new class of chiral device that exhibits dual mode motions in response to two different external stimuli.

Experimental Section

H_2L1: A solution of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (WSC·HCl) (1.81 g, 9.46 mmol) in DMF (90 mL) was added at 0 °C to a solution of *N,N'*-ethylene-bis(*N*-methyl-(*s*)-alanine) (**1**;[19] 1.00 g, 4.30 mmol) and 1-hydroxybenzotriazole hydrate (HOBt·H_2O) (1.45 g, 9.46 mmol) in DMF (60 mL), and the solution was stirred for 30 min. A solution of 2,5-dimethoxyaniline (1.45 g, 9.46 mmol) in DMF (2 mL) was added, and the solution was stirred overnight, during which time the temperature of the solution was allow to rise to room temperature (Scheme 1). After the solvent was removed in vacuo, the residue was dissolved in chloroform (30 mL) and washed with saturated Na_2CO_3 aqueous solution (3 × 10 mL), then the organic phase was dried over anhydrous Na_2SO_4. The solution was evaporated, and the product was purified by chromatography on silica gel by using toluene/chloroform/ethyl acetate (4/4/1) as eluent, and then recrystallized from methanol to give colorless H_2**L1** as a single crystal (yield: 1.55 g, 3.08 mmol; 72 %). The ^1H and ^{13}C NMR spectra indicated its stereochemical purity to be greater than 98 % *de*. M.p. 161–162 °C; $[\alpha]_D^{28} = +85.5$ ($c = 0.534$ in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 9.84$ (s, 2H; NH), 8.13 (d, $J = 2.93$ Hz, 2H; 6-Ar), 6.60 (d, $J = 8.94$ Hz, 2H; 3-Ar), 6.46 (dd, $J = 2.93$, 8.94 Hz, 2H; 4-Ar), 3.76 (s, 6H; OCH_3), 3.67 (s, 6H; OCH_3), 3.38 (q, $J = 6.97$ Hz, 2H; α-H), 2.65 (m, 2H; ethylene), 2.53 (m, 2H; ethylene), 2.28 (s, 6H; NCH_3), 1.30 ppm (d, $J = 6.97$ Hz, 6H; β-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 171.8$ (C=O), 153.5 (Ar), 142.3 (Ar), 128.0 (Ar), 110.2 (Ar), 108.3 (Ar), 105.3 (Ar), 64.8 (α-C), 55.8 (OCH_3), 55.7 (OCH_3), 51.8 (ethylene), 39.1 (NCH_3), 8.58 ppm (β-CH_3); IR (KBr): $\tilde{\nu} = 3269$ (s, NH), 1682 cm^{-1} (s, C=O); FAB-MS (NBA): *m*/*z*: 503.4, calcd for $[M+H]^+$: 503.3; elemental analysis calcd (%) for $C_{26}H_{38}N_4O_6$: C 62.1, N 11.1, H 7.62; found: C 62.1, N 11.0, H 7.60.



Scheme 1. Synthesis of H_2**L1**.

[Co(H_2L1)(CF_3SO_3)(H_2O)](CF_3SO_3)·($CHCl_3$): A solution of Co(CF_3SO_3)$_2$·5H_2O (44.7 mg, 0.100 mmol) in acetonitrile (5 mL) was added to H_2**L1** (50.7 mg, 0.100 mmol) and the solution was stirred for 1 h at room temperature. The solvent was evaporated, and a pink single crystal suitable for X-ray structure analysis was isolated from the chloroform solution (3 mL) on layering with toluene (2 mL) (yield 72.1 g, 0.0723 mmol; 72 %). M.p. 208–209 °C; $[\alpha]_D^{27} = +44.5$ ($c = 0.210$ in CH_3CN); IR (KBr): $\tilde{\nu} = 3406$ (s, NH), 1636 cm^{-1} (s, C=O); FAB-MS (NBA): *m*/*z*: 710.2, calcd for $[Co(H_2\mathbf{L1})(CF_3SO_3)]^+$: 710.2; elemental analysis calcd (%) for $C_{29}H_{41}Cl_3CoF_6N_4O_{13}S_2$: C 34.93, N 5.62, H 4.14; found: C 34.92, N 5.57, H 4.20.

[Co(L1)]: A solution of $Co(ClO_4)_2 \cdot 6H_2O$ (224 mg, 0.639 mmol) in acetonitrile (4 mL) was added to H_2**L1** (292 mg, 0.581 mmol), and the solution was stirred for 1 h at room temperature. $(C_2H_5)_3N$ (235 mg, 2.32 mmol) was added and the mixture was left to stand overnight, which led to the formation of green microcrystals of the title complex (yield 307 g, 0.549 mmol; 94 %). Single crystals suitable for an X-ray structure analysis were obtained from a solution of the complex in methanol. M.p. > 300 °C; $[\alpha]_D^{27} = +315$ ($c = 0.205$ in $CHCl_3$); IR (KBr): $\tilde{\nu} = 1614$ cm^{-1} (s, C=O); FAB-MS (NBA): *m*/*z*: 559.2, calcd for $[Co(\mathbf{L1})]^+$: 559.2; elemental analysis calcd (%) for $C_{26}H_{36}CoN_4O_6$: C 55.81, N 10.01, H 6.49; found: C 55.60, N 9.91, H 6.45.

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Keywords: chirality · helical structures · molecular devices · N,O ligands · supramolecular chemistry

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[9] X-ray diffraction data were collected on a pink crystal of [Co(H_2**L1**)(CF_3SO_3)(H_2O)](CF_3SO_3)·($CHCl_3$) (0.30 × 0.10 × 0.10 mm) and a green crystal of [Co(**L1**)] (0.30 × 0.25 × 0.10 mm) on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated

$Mo_{K\alpha}$ radiation ($\lambda = 0.71070$ Å) to a $2\theta_{max}$ of 50.0°. Data were processed on a PC using CrystalClear software (Rigaku). The crystal structures were solved by direct methods by using SIR-97 (A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115–119) and refined by full-matrix least squares on F^2 using SHELXL-97 (G. M. Sheldrick, SHELXL-97; University of Göttingen: Göttingen, Germany, **1997**). All hydrogen atoms except for those in the coordinating water molecule were placed at ideally geometrical positions. Non-hydrogen atoms were refined anisotropically. The absolute configuration for each complex was determined by the configuration of the ligand and Flack parameter. CCDC-670887 and CCDC-670888 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[10] X-ray data for [Co(H$_2$**L1**)(CF$_3$SO$_3$)(H$_2$O)](CF$_3$SO$_3$)·(CHCl$_3$): $C_{29}H_{41}Cl_3CoF_6N_4O_{13}S_2$, $M_r = 997.06$, orthorhombic, space group $P2_12_12$, $a = 16.9306(11)$, $b = 28.5388(17)$, $c = 8.8285(5)$ Å, $V = 4265.7(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.553$ g cm^{-3}, $\mu = 0.776$ mm^{-1}, $T = 100(2)$ K, $F(000) = 2044$, 27108 reflections collected, of which 7390 were unique ($R_{int} = 0.0506$). Final R indices [7094 observed reflections, $I > 2\sigma(I)$]: $R_1 = 0.0547$, $wR_2 = 0.1130$. GOF = 1.271, Flack parameter = 0.021(19). Highest residual electron density 0.688 e Å^{-3}.

[11] CD spectra of [Co(H$_2$**L1**)(CF$_3$SO$_3$)(H$_2$O)](CF$_3$SO$_3$)·(CHCl$_3$) as a KBr pellet exhibited a positive signal around 530 nm (see Figure S1 in the Supporting Information), the sign of which was the same as that observed in solution in CH$_3$CN/CHCl$_3$ (1/9).

[12] The ^{19}F NMR spectrum of [Co(H$_2$**L1**)(CF$_3$SO$_3$)(H$_2$O)](CF$_3$SO$_3$)·(CHCl$_3$) in CD$_3$CN/CDCl$_3$ (1/9) showed only one signal at $\delta = 8.65$ ppm versus CFCl$_3$, which could be assigned to a free CF$_3$SO$_3^-$ ion. The intensity of the signal fit for one CF$_3$SO$_3^-$ ion, suggesting that one CF$_3$SO$_3^-$ ion on average coordinated to the Co^{II} center (see Figure S3 in the Supporting Information).[20]

[13] IR spectra of [Co(H$_2$**L1**)(CF$_3$SO$_3$)(H$_2$O)](CF$_3$SO$_3$)·(CHCl$_3$) in CD$_3$CN/CHCl$_3$ (1/9) showed the existence of free CF$_3$SO$_3^-$ and coordinated CF$_3$SO$_3^-$ ions (see Figure S4 in the Supporting Information).[21]

[14] The paramagnetic ^{1}H NMR spectrum of [Co(H$_2$**L1**)(CF$_3$SO$_3$)(H$_2$O)]-(CF$_3$SO$_3$)·(CHCl$_3$) in CD$_3$CN/CDCl$_3$ (1/9) revealed the presence of three different species, two of which have independent C_2-symmetrical patterns (see Figure S5 in the Supporting Information). One of these species has an NMR spectrum similar to that observed in CD$_3$CN, in which none of the CF$_3$SO$_3^-$ ion coordinates directly to the Co^{II} center. The other two species could be assigned as the Λ *cis*-α complexes, in which one or two CF$_3$SO$_3^-$ ions coordinated to the Co^{II} center, since the CD intensity of the complex in this mixed solvent is similar to that obtained in CH$_3$CN.

[15] X-ray data for [Co(**L1**)]: $C_{26}H_{36}CoN_4O_6$, $M_r = 559.52$, orthorhombic, space group $P2_12_12_1$, $a = 12.1381(8)$, $b = 11.9435(7)$, $c = 18.0180(10)$ Å, $V = 2612.1(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.423$ g cm^{-3}, $\mu = 0.705$ mm^{-1}, $T = 100(2)$ K, $F(000) = 1180$, 16355 reflections collected, of which 4479 were unique ($R_{int} = 0.0273$). Final R indices [4419 observed reflections, $I > 2\sigma(I)$]: $R_1 = 0.0542$, $wR_2 = 0.1636$. GOF = 1.181, Flack parameter = 0.05(3). Highest residual electron density 0.425 e Å^{-3}.

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[17] Since the H$_2$**L2**-Co(ClO$_4$)$_2$ complex did not provide such a green species upon addition of a proton sponge, coordination of methoxy oxygen atoms was essential to stabilize a contracted form.

[18] The ^{1}H NMR spectrum of this complex after extension by CF$_3$SO$_3$H clearly showed that almost complete inversion of helicity (Δ/Λ form = 75/25) was achieved. Upon addition of two equivalents of a proton sponge, the CD spectrum was restored to the characteristic pattern of the contracted [Co(**L1**)] complex (see Figure 3, ○).

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